

ELECTROLESS PLATING BATH OF RHODIUM OR RHODIUM ALLOY

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Equivalents: JP1258018C, JP59039504B

Abstract

PURPOSE:To provide a titled plating bath which has high stability, offers a high utilizing rate of metal, and is high in plating speed by using rhodium or the other metal as ammine complex salt together with rhodium and contg. hydroxyl amine salt and hydrazine therein.

CONSTITUTION:Ammine complex salt of rhodium or a mixture thereof and the other ammine complex salt, hydroxyl amine salt as a stabilizer and hydrazine as a reducing agent are incorporated and the pH thereof is controlled to 10-13, whereby an electroless plating bath of rhodium or a rhodium alloy is obtained. Rhodium salt or hexaammine salt or the like obtd. by causing the mixture of said salt and the salt of the other metal such as platinum to react with ammonia is preferable as the ammine complex salt. Water-soluble hydrochloride or the like is preferable as the hydroxyl amine salt and hydrazine hydrate or the like which forms hydrazine in the state of an aq. soln. is preferably usable for the hydrazine.

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Bibliographic Information

Electroless baths for coating with rhodium or rhodium alloys. (Agency of Industrial Sciences and Technology, Japan). Jpn. Kokai Tokkyo Koho (1983), 6 pp. CODEN: JKXXAF JP 58204168 A2 19831128 Showa. Patent written in Japanese. Application: JP 82-85535 19820519. CAN 100:160724 AN 1984:160724 CAPLUS

Abstract

The coating baths at a pH of 10-13 contain (1) ammine complex salt of Rh, (2) hydroxylamine salt stabilizing agent, and (3) hydrazine as reducing agent. The baths are stable, rapidly deposit Rh or Rh alloys, and efficiently utilize the bath constituents. Thus, a Cu plate was (1) degreased by alk. cleaning, (2) immersed at room temp. for 10-20 s in aq. 3 wt.% HCl, (3) activated by immersing 30 s in aq. 2 N HCl soln. contg. 5 wt.% PdCl₂, (4) water rinsed, (5) coated with Rh by immersing 2 h at 70-80° in a bath contg. Rh(NH₃)₆Cl₃ 0.12%, NH₂OH.HCl 0.1 g, N₂H₄.H₂O 2 mL, NH₄OH 10 mL, and 100 mL H₂O at a pH of 11.5. The resulting Rh coating was .apprx.2 μ thick.

Patent Classifications

IPC: C23C003-02.

Indexing -- Section 56-6 (Nonferrous Metals and Alloys)

Coating process

(electroless, with rhodium and rhodium alloys, bath for)

Rhodium alloy

(coating with, bath for electroless)

302-01-2, uses and miscellaneous

Japan Patent Office

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Electroless plating bath of rhodium and rhodium alloy

Patent Application No. 85535 - 1982

Date of Application : May 19, 1982

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Specification

Title of Invention : Electroless plating bath of rhodium and rhodium alloy

Claims of the Patent

(1) Electroless plating bath of rhodium and rhodium alloy, which is characterized by that it contains (a) the ammine complex salt of rhodium or the mixture of this and the ammine complex salt of other metals, (b) hydroxyl amine salt and (c) hydrazine and that its pH is 10 ~ 13.

Detailed Description of the Invention

This invention is related to the hydrazine type plating bath for the electroless plating of rhodium or rhodium alloy on the surface of metal or non-metal. Specifically, it is related to a novel plating bath which has excellent stability of the bath solution, has high ratio of utilization of the rhodium or rhodium alloy and also has high rate of plating.

Generally, for the chemical plating of rhodium or rhodium alloy, one uses the mixed solution of their metallic salt and ethylene diamine (which forms the amine complex salt) and ammonia into which, as the reducing agent, hydrazine, sodium borohydride or alkyl amine borane has been added. However, with the said composition alone, the stability of amine complex salt in the bath solution is poor and the

reduction of rhodium or rhodium alloy proceeds too much and it separates out (i.e. undergoes self decomposition) into the bath and, therefore, a stabilizer for the suppression of reaction is added commonly. Currently, however, even in the case of having the stabilizer added, a bath solution having sufficient stability has not yet been obtained.

On the other hand, when seen from the view point of practical uses, the rhodium itself is expensive and so it is desirable that, in addition to the smaller self decomposition in the bath solution, the ratio of separating out from other metallic salt is high. In other words, it is ideal that, in each batch of the plating process, the rhodium contained is used completely.

Further, when seen from the standpoint of process operability, it is desirable that the time for separating out is fast.

The present inventors conducted additional tests of the known plating methods with the consideration of the above said requirements, i.e. (1) Stability of the bath solution, (2) Utilization ratio of rhodium, and (3) Plating rate and a satisfactory bath solution has not been found out at all.

Thus, although the stabilizer was being used, in the bath which uses the borohydride salt as the reducing agent, (1) and (2) were poor and, in the bath solution which uses alkyl amine borane, (2) and (3) were poor. In the hydrazine bath, (1) was unstable. However, the two former ones showed no room for improvement even when the bath solution composition was varied and tried in various manner while, for the hydrazine bath, it was found that the improvement of (1) can be expected with the improvement of the bath solution.

In all cases of the method of using hydrazine as the reducing agent in the chemical plating of rhodium, the solution consisting of rhodium chloride, sulfate, ethylene amine, sodium hydroxide is used and, as the reducing agent, hydrazine salt alone or combined with the borohydride salt is used and, further, as the stabilizer, potassium ferro cyanide (Chemical Abstract Vol. 86, 94262 n), diimethyl glyoxime (Chemical Abstract Vol. 86, 45620 y, Vol. 87, 27154 m) are used.

Actually, however, when rhodium was grown on the surface of metal, plastics or ion exchange membrane in these known bath solution and under the plating condition, some of the

above said (1), (2) and (3) was inadequate and there was no satisfactory case. Also, the ethylene diamine itself which is present in the base bath, also, can not be used in the case of rhodium plating which is conducted for the purpose of bonding catalyst electrode to the ion exchange membrane because it causes the contamination of the membrane.

In order to obtain a plating bath which is excellent to all of the said (1), (2) and (3) in the hydrazine type plating bath, the present inventors energetically investigated the reagents and compatible stabilizers and, as the result, found out that, when the rhodium or the metal of the alloy composition which is to be bonded is used in the form of the ammine complex salt solution and, also, as the stabilizer, hydroxyl amine salt is used, the desired objective can be satisfied. Thus, this invention was accomplished.

Thus, this invention is related to the electroless plating bath of rhodium and rhodium alloy, which is characterized by that it contains (a) the ammine complex salt of rhodium or the mixture of this and the ammine complex salt of other metals, (b) hydroxyl amine salt and (c) hydrazine and that its pH is 10 ~ 13.

As for the rhodium ammine complex salt in this invention, it is preferred to use, for example, the hexa ammine salt $[\text{Rh}(\text{NH}_3)_6]\text{X}_3$ (X is a halogen, NO_2 , etc.) that is obtained by placing rhodium salt and ammonia water together in an autoclave and conducting the reaction under a pressure of 10 ~ 30 Kg/cm² at a temperature of 120 ~ 160 deg C for 3 ~ 12 hours. But, one can also use the solution obtained by boiling the rhodium salt and ammonia water together until the color becomes thin yellow while ammonia water is being added additionally.

In the case of plating the rhodium alloy, it is preferred to treat the mixed salt of the salts of rhodium, platinum, rutheniums, iridium, nickel and cobalt similarly with the hot ammonia water under pressurization and use it as a stable mixed ammine salt complex solution. At this time, the mol ratio of the metal being added relative to rhodium is 0.1 ~ 1.0 mols with respect to 1 mol of rhodium; in the case of more than 3 elements, also, it is preferred that the number of mols of the total of added metals with respect to 1 mol of rhodium is less than 1 mol. Showing an example of the case of 2 elements, for example in the case of platinum or iridium, it is preferably 0.1 ~ 0.5 mol and, in the case of ruthenium, nickel or cobalt, it is preferably 0.1 ~ 1

mol.

As for the hydroxyl amines which are used in this invention, a water-soluble salt, e.g. hydrochloride, sulfate, nitrate, etc. are preferred.

As for the hydrazine in this invention, the one which becomes hydrazine in the state of water solution, e.g. the hydrate, hydrochloride, sulfate of hydrazine, can be used suitably.

The solution composition of this invention is as follows: As the rhodium or rhodium alloy, the ammine complex salt is 0.001 ~ 0.1 M/ liter (0.1 ~ 10 g/ liter in the case of rhodium), preferably 0.001 ~ 0.05 M/ liter (0.1 ~ 5 g/ liter in the case of rhodium), the hydroxyl amine is 0.003 ~ 1.5 M/ liter (0.1 ~ 50 g/ liter), preferably 0.003 ~ 0.15 M/ liter (0.1 ~ 5 g) and the hydrazine is 0.003 ~ 1.5 M/ liter (1 ~ 50 g/ liter in the case of hydrazine mono hydrate), preferably 0.003 ~ 0.3 M/ liter (1 ~ 10 g/ liter in the case of hydrazine mono hydrate). In this invention, the solution of the above said composition is used with the pH adjusted, by using ammonia water or alkaline pH buffer solution, in the range of 10 ~ 13, preferably 11 ~ 12.

If the pH is higher than 13, the rate of reduction becomes fast and the self decomposition increased. Also, if the pH is lower than 10, the growth rate is small and the plating time becomes long. If the hydroxyl amine is greater than 50 g/ liter, the growth is suppressed extremely and the plating can not proceed.

The plating bath of this invention is very stable compared to the rhodium ion (Rh^{3+} , $(\text{RhCl}_6)^{3-}$, $[\text{Rh}(\text{NH}_2\text{C}_2\text{H}_4\text{NH}_2)_3]^{3+}$, etc) in the aqueous solution or alkaline solution of ammine complex ion in the bath solution $[\text{Rh}(\text{NH}_3)_6]^{3+}$ is RhCl_3 or $\text{Rh}_2(\text{SO}_4)_3$ (same in the case of rhodium alloy) and, when the hydroxyl amine salt is added, more stable complex is formed and the self decomposition is suppressed mostly.

For this reason, the plating bath of this invention exhibits very good stability without self decomposition over a long time when the material to be plated is not dipped.

At the time point when the material to be plated is dipped, the reductive reaction starts catalytically and the plating proceeds selectively but this continues until the rhodium or rhodium alloy in the bath solution is consumed to

a high ratio of more than 95 %. Plating time depends on the shape of the material to be plated also and so it is not fixed but, taking the example of obtaining the plated layer of 3 μ , it is a short time of 1.5 ~ 2 hours.

For an example of the plating bath of this invention and the known hydrazine type plating bath, the comparison is shown in Table 1.

Table 1

第 1 表				
A	B	C	D	E
処 法	浴液のみ 80℃放置	銅板へメ ッキした ときの所 見	イオン交 換膜上へ のロジウ ムの成長	文 献
1 $Rh_2(SO_4)_3$ 、0.34 g/lとして0.34 g/l				
2 エチレンジアミン 12	2hr以内	メッキ厚小	成長不良	ケミカルア ストラクト 86巻
3 $NaOH$ 25	分 解	浴液分解	浴液分解 多い	94262
4 $K_2P_2(CN)_6 \cdot 3H_2O$ 10				
5 $N_2H_4 \cdot H_2O$ 100 60-70				
6 $RhCl_3$ 2-20 g/l				
7 $NiCl_2$ 2-20				
8 $N_2H_4 \cdot H_2O$ 2-200	2hr以内	メッキ厚小	成長性と んどせず	ケミカルア ストラクト 86巻
9 $NH_2CH_2CH_2NH_2$ 8-80	分 解	浴液分解 多い	浴液分解 多い	46520 y
10 ジメチルグリオキシル 8-25				
11 $NaOH$ 20-110				
12 $NaBH_4$ 0.25-1.0				

A	B	C	D	E
処 法	浴液のみ 80℃放置	銅板へメ ッキした ときの所 見	イオン交 換膜上へ のロジウ ムの成長	文 献
13 $RhCl_3$ 0.0071 mol/l				
14 $NiCl_2$ 0.025				
15 $NaOH$ 1.0	2hr以内	メッキ厚小	成長不良	ケミカルア ストラクト 87巻
16 ジメチルグリオキシル 0.086	分 解	浴液分解 多	浴液分解 多	27154
17 エチレンジアミン 0.4				
18 N_2H_4 0.4				
19 $NaBH_4$ 0.026M				
20 $[Rh(NH_3)_6]Cl_3$ ロジウムとして 3 g/l				
21 $NH_2OH \cdot HCl$	8時間 以 上	メッキ 良 好	成長良好	本発明 メッキ浴
22 $N_2H_4 \cdot H_2O$	安 定	浴液分解 な	浴液分解 な	
23 NH_4OH				

A. Treatment method; B. Bath solution alone, left at 80 deg C; C. Observation at the time of plating copper plate; D. Growth of rhodium on the ion exchange membrane; E. Literature;

1. $Rh_2(SO_4)_3$, 0.34 g/ liter as rhodium; 2. Ethylene diamine, 12 g/ liter; 10. Dimethyl glyoxime 8 ~ 25 g/ liter; 16. Dimethyl glyoxime 0.086 mol / liter; 17. Ethylene diamine 0.4 mol/ liter; 20. $[Rh(NH_3)_6]Cl_3$, 3 g/ liter as rhodium; (Table 1 continued to the next page)

(Table 1 continued from the previous page)

Column B

1 ~ 5, 6 ~ 12, 13 ~ 19. Decomposition within 2 hr. ; 20 ~ 23. Stable for more than 8 hours

Column C

1 ~ 5. Plated thickness is small, decomposition of the bath solution; 6 ~ 12, 13 ~ 19. Plated thickness is small, much decomposition of the bath solution; 20 ~ 23. Good plating, no decomposition of the bath solution

Column D

1 ~ 5. Growth is poor, much decomposition in the bath solution; 6 ~ 12. Almost no growth, much decomposition in the bath solution; 13 ~ 19. Growth is poor, much decomposition in the bath solution; 20 ~ 23. Growth is good, no decomposition of the bath solution

Column E

1 ~ 5. Chemical Abstract, Vol. 86, 94262 n; 6 ~ 12. Chemical Abstract, Vol. 86, 46520 y; 13 ~ 19. Chemical Abstract Vol. 87 27154 m; 20 ~ 23. Plating bath of this invention

As is clear from Table 1, it is seen that the plating bath of this invention has very good stability of the bath solution and selectivity to the material to be plated.

Examples of the materials to which the plating bath of this invention can be applied are: metal, e.g. copper, nickel, iron, and their alloys, titanium, tantalum, electronic parts or the industrial materials such as electrodes. It can be applied also to the common materials such as synthetic resin, glass and ceramics to which the electroless plating is possible. Further, the plating bath of this invention contains the ionic active substance such as ethylene diamine and dimethyl glyoxime and so it is particularly good as the solution in bonding the rhodium or rhodium alloy to the ion exchange membrane and it can be applied as the technology of preparing the bonded body in which the electrodes are bonded to the membrane surface of the solid polymeric electrolyte (ion exchange membrane) which has recently been used in the electrolysis of aqueous solution.

In all cases, it is preferred to conduct an activation treatment in advance to the material to be plated.

In the case of metals, the surface is dipped in a solu-

tion of salt such as palladium, platinum, rhodium and, when necessary it is also dipped in the water solution of boron hydride salt to activate and then it is dipped in the plating bath of this invention.

In the cases of polymer, glass, ceramics, also, normally the surface hydrophilization, sensitizing treatment and activation treatment which are commonly used in the cases of chemical plating of the copper or nickel on the surface of these materials are conducted and the material is dipped in the plating bath of this invention.

Also, in the case of ion exchange membrane, first the metal salt solution (ammine complex salt is preferred) is let to be adsorbed after the roughening of the surface and next the reduction is conducted by the solution of sodium borohydride to bond the first layer of 1 ~ 2 μ and, after this, it is dipped in the plating bath of this invention and the growth is let to occur.

Plating temperature is 50 ~ 90 deg C in all cases and preferably the plating is conducted at 60 ~ 75 deg C.

As to the plating thickness, an amount of rhodium or rhodium alloy which is needed on the basis of the surface area of the said plating body which was determined in advance is let to be present in the solution and then the plating is conducted. Utilization ratio of the rhodium or rhodium alloy in the solution is high at over 95 % and the small amount of rhodium remaining in the used solution can be recovered by adding the borohydride salt for precipitation.

The plated layer by this invention has equal electric characteristics and mechanical strength in comparison to the electric plating so this plating is suitable for the plating of the plating body of complex shape and in the plating of small sized electronic parts, electrical contact point, non-magnetic or magnetic rhodium alloys.

Also, it can be utilized as a plating method in the case of making ion exchange membrane - electrode bond for use in the electrolysis of aqueous solution or for use in fuel cell as the industrial material.

In the following, the invention is explained in further detail by using the examples of application.

Example of Application 1

To 5 g of RhCl_3 , 50 ml of 28 % NH_4OH was added and, in an autoclave, under 20 Kg/cm^2 at 150 deg C, a treatment was conducted for 12 hours. After this, it was taken out and it was filtered while it was hot and the filtrate was concentrated to crystallize out the hexa ammine rhodium (III) chloride. Using this, the plating bath of the invention having the following composition was prepared.

$[\text{Rh}(\text{NH}_3)_6] \text{Cl}_3$	0.12 g
$\text{NH}_2\text{OH} \cdot \text{HCl}$	0.1 g
$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$	2 ml
NH_4OH (28 %)	10 ml
Water total amount	100 ml
pH	11.5
Bath temperature	70 ~ 80 deg C

Using the above described solution, plating was conducted on a copper plate.

Sample copper plate (2 x 4 cm) was degreased with alkali and this was dipped in hydrochloric acid (3 %) at room temperature for 10 ~ 20 seconds. Next, this was dipped in 5 % PdCl_2 solution in 2N - HCl at room temperature for 30 seconds to activate. After washing with water, this was dipped in the above said plating bath solution for 2 hours to obtain the rhodium plating of about 2 μ thickness.

Precipitation into the bath solution or deposit on the vessel wall was not observed. After the treatment, the rhodium residue in the bath solution was less than 1 mg and the rhodium utilization ratio was over 98 %.

Example of Application 2

RhCl_3 and NH_4OH were boiled for 3 hours to obtain ammine complex ion $[\text{Rh}(\text{NH}_3)_6]^{3+}$ solution. This was used to prepare the bath solution of the following composition.

$[\text{Rh}(\text{NH}_3)_6]^{3+}$ solution	0.04 g as rhodium
$\text{NH}_2\text{OH} \cdot \text{HCl}$	0.5 g
$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$	2.5 ml
Buffer solution of pH12 (0.1 M/liter NaOH + 0.1 M/liter $\text{Na}_2\text{B}_2\text{O}_7$)	10 ml
Water total amount	100 ml
pH	12.0
Bath temperature	70 ~ 80 deg C

Using the above described solution, rhodium plating was

conducted on the ABS resin (.3 x 3 cm test piece).

In the pretreatment of sample, the following solution was used as in the common case of conducting plating on plastics.

Etching bath

H ₂ SO ₄	550 ml
CrO ₃	20 g
H ₂ O (total amount)	1000 ml

Etching was conducted at 65 deg C for 20 minutes and then washing was done with water.

Catalyst bath

Palladium chloride	0.3 g
Stannous chloride	15 g
Hydrochloric acid (35 %)	250 ml
Water (total amount)	1000 ml

In the above described bath solution, at 30 deg C, it was dipped for 3 minutes.

Activation bath

Sodium borohydride	0.5 g
Water, total amount	1000 ml

In the activation bath, at room temperature, treatment was done for 2 minutes.

In continuation, dipping was done in the rhodium plating bath for 30 minutes and a glossy rhodium plating of about 0.5 u was obtained. The rhodium plating bath was used repeated for 3 times with the use of same type of samples and, for each sample, similar rhodium plating was obtained. During this period, the bath solution was stable and decomposition did not occur.

Example of Application 3

Using the ion exchange membrane based on the perfluoro sulfonic acid [made by duPont Co., Naph Ion 117 membrane, membrane thickness 7 mils (about 0.175 mm)], rhodium was bonded to the circular membrane of diameter 80 mm.

For the pretreatment of membrane, first, roughening was done by sand blast and, after this, boiling was done with 4N - HCl for deionization and then washing was done with water. Next, this was dipped (room temperature, 5 hours) in the rhodium ammine complex salt $[\text{Rh}(\text{NH}_3)_6]^{3+}$ solution which was prepared as in Example of Application 1. After washing with water, in the 0.05 % ammoniacal solution of NaBH_4 , reduction was conducted at 40 ~ 60 deg C to let rhodium layer of 1 ~ 1.5 u deposit. In the growth of this rhodium layer, the solution of following composition was used.

$[\text{Rh}(\text{NH}_3)_6]^{3+}$ solution	0.3 g as rhodium
$\text{NH}_2\text{OH} \cdot \text{HCl}$	0.5 g
$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$	1.0 ml
NH_4OH (28 %)	10 ml
Water total amount	150 ml
pH	11.5 ~ 11.8
Bath temperature	70 ~ 80 deg C

The plating treatment was conducted for 2 hours and, after the treatment, the rhodium layer grew to a thickness of about 5 u. Decomposition in the bath solution was not observable and the utilization ratio of rhodium was 99 %.

Example of Application 4

RhCl_3 and PtCl_4 were mixed by a Pt/Rh mol ratio of 0.5/1.0 and, together with ammonia water, this was placed in an autoclave and, under 20 Kg/ cm^2 , at 160 deg C, treatment was conducted for 10 hr to prepare the ammine complex salt mixture and this was used.

Pt - Rh mixed ammine complex salt	0.1 g as rhodium
$\text{NH}_2\text{OH} \cdot \text{HCl}$	2.0 g
$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$	4 ml
NH_4OH (28 %)	20 ml
Water total amount	200 ml
pH	11.8

Nickel sample plate (5 x 5 cm) was degreased with alkali and, by using the solution of RhCl_3 2 g, HCl 10 ml, water total amount 1 liter, activation treatment was conducted. After washing with water, this was dipped in the above said plating bath and, at 70 deg C, plating treatment was conducted for 2 hr.

On the nickel surface, about 3 u thick rhodium - platinum alloy was obtained and the utilization ratio of rhodium and

platinum was over 95 %.

Letter of Revision to the Proceeding (Self initiated)

July 2, 1983

To: K. Wakasugi, Director General of Patent Office

1. Indication of the Case
1982 Patent Application No. 85535
2. Title of Invention
Electroless plating bath of rhodium and rhodium alloy
3. Person Making the Revision
Relation to the case: Patent Applicant
Address: 3-1 1-Chome, Kasumigaseki, Chiyoda Ku, Tokyo
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Name: Director, Osaka Industrial technology Laboratory
I. Naitoh
5. Date of the Order of Revision
Self initiated
6. Object of the Revision
[Detailed descripton of the invention] in the specific-
tion
7. Content of the Revision
As shown below

Content of the Revision
(Page and line numbers refer to the translation)

1. Specification, p. 3, line 27. [at the temperature of 120 deg C ~ 160 deg C] is revised to [at the temperature of 110 ~ 160 deg C].
2. Specification, p. 3, line 23 ~ line 24. [hexa ammine salt $[\text{Rh}(\text{NH}_3)_6]\text{X}_3$ (X is a halogen, NO_2 , etc.)] is revised to [[hexa ammine salt $[\text{Rh}(\text{NH}_3)_6]\text{X}_3$ or penta ammine salt $[\text{Rh}(\text{NH}_3)_5 \text{X}] \text{X}_2$ (X is a halogen, NO_2 , etc.)]
3. Specification, p. 4, line 15 ~ line 16. [1 ~ 50 g/

liter] is revised to [0.15 ~ 75 g/ liter].

4. Specification, p. 4, line 17. [1 ~ 10 g/ liter] is revised to 0.15 ~ 15 g/ liter].

5. Specification, p. 4, line 11 from bottom. [[Rh (NH₃)₆]³⁺ is RhCl₃] is revised to [[Rh (NH₃)₆]³⁺, [Rh (NH₃)₇Cl]³⁺, [Rh (NH₃)₇ H₂O]³⁺ are RhCl₃].

6. Specification, p. 8, line 11 from bottom. [Rh (NH₃)₆]³⁺ solution] is revised to [mixed solution of Rh (NH₃)₆]³⁺ and [Rh(NH₃)₆H₂O]³⁺].

7. Specification, p. 8, line 9 from bottom. [Rh (NH₃)₆]³⁺ solution] is revised to [rhodium ammine complex salt solution].

8. Specification, p. 10, line 11. [[Rh (NH₃)₆]³⁺ solution] is revised to [rhodium ammine complex ion solution].

laser printer rotating mirror is metalized, coated with a metal, mirror surface-finished, and coated with another metal by vapor deposition. Thus, a multi-sided ceramic base was coated with a mixt. contg. Mo 82, Mn 15, and Ti 3%, sintered at 1450° in a H furnace, coated with 100 μ -thick Ni, polished, and coated with Al by vapor deposition to form reflection surfaces having reflectivity 90%.

100: 160723z Corrosion prevention of electric conductors in electronic parts. Hitachi, Ltd. Jpn. Tokkyo Koho JP 58 47,853 [83 47,853] (Cl. H01L21/60), 25 Oct 1983, Appl. 75/130,419, 31 Oct 1975; 6 pp. In the formation of a corrosion-resistant protective film on Al conductor surfaces of electronic parts, the bonding parts of the Al conductors are precoated with chem.-resistant film, and treated with an aq. soln. contg. H_2CrO_4 , H_3PO_4 , and F compds. Thus, the bonding part of an Al conductor was coated with a photo-resist film mask, the Al conductor was treated in a soln. contg. H_3PO_4 10-300, H_3CrO_4 6 g/L, and F/ CrO_3 ratio 0.03-0.6 at 20-50° for 1-5 min to form a corrosion-resistant film.

100: 160724a Electroless baths for coating with rhodium or rhodium alloys. Agency of Industrial Sciences and Technology Jpn. Kokai Tokkyo Koho JP 58,204,168 [83,204,168] (Cl. C23C3/02), 28 Nov 1983, Appl. 82/85,535, 19 May 1982; 6 pp. The coating baths at a pH of 10-13 contain (1) ammine complex salt of Rh, (2) hydroxylamine salt stabilizing agent, and (3) hydrazine as reducing agent. The baths are stable, rapidly deposit Rh or Rh alloys, and efficiently utilize the bath constituents. Thus, a Cu plate was (1) degreased by alk. cleaning, (2) immersed at room temp. for 10-20 s in aq. 3 wt.% HCl, (3) activated by immersing 30 s in aq. 2 N HCl soln. contg. 5 wt.% $PdCl_2$, (4) water rinsed, (5) coated with Rh by immersing 2 h at 70-80° in a bath contg. $Rh(NH_3)_6Cl_3$ 0.12%, $NH_2OH.HCl$ 0.1 g, $N_2H_4.H_2O$ 2 mL, NH_4OH 10 mL, and 100 mL H_2O at a pH of 11.5. The resulting Rh coating was $\sim 2 \mu$ thick.

100: 160725b Wear-resistant alloys with multilayer coatings. Hitachi Metals, Ltd. Jpn. Kokai Tokkyo Koho JP 58,217,479 [83,217,479] (Cl. C04B41/06), 17 Dec 1983, Appl. 82/98,280, 08 Jun 1982; 3 pp. WC-base hard alloys, TiC-base cermets, or TiN-base cermets are coated with TiC and TiB_2 alternately in ≥ 8 layers of 2-15 μ total thickness by chem. vapor deposition. Thus, a WC-6% Co alloy [11136-82-6] cutting-tool tip was coated with TiC and TiB_2 alternately to a total thickness of 6 μ (single layer thickness 0.1 μ) and used for cutting SCN3 at 200 m/min. The service life was 35 min, compared to 10 when it was coated with 3 μ -thick TiC and 3 μ -thick TiB_2 .

100: 160726c Volume-combining type glow-discharge apparatus. Kyoto Ceramic Co., Ltd. Kawamura, Takao Jpn. Kokai Tokkyo Koho JP 58,217,672 [83,217,672] (Cl. C23C11/00), 17 Dec 1983, Appl. 82/100,079, 10 Jun 1982; 7 pp. Elec. conducting drums are coated with amorphous Si photosensitive films in a vol.-combining type glow-discharge app. having a pair of arc electrodes equipped with a center nozzle slit. The drum is placed between the electrode arcs and a SiH_4 -contg. gas stream is injected through 1 nozzle slit, swept through the drum surface, and suctioned into the other slit in the other electrode. Thus, an Al-alloy drum was coated with a